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硕 士 学 位 论 文

微波介质陶瓷 $Ba_5Nb_4O_{15}$ 的低温烧结和 MCT 凝胶注模成型的工艺研究

Low-temperature Sintering of $Ba_5Nb_4O_{15}$-based Microwave Dielectric Ceramics and Gel-casting of MCT ceramics

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摘 要

本论文采用传统的固相法低温制备 $Ba_5Nb_4O_{15}$ 陶瓷，研究了烧结助剂、B 位离子取代和工艺因素对陶瓷结构与介电性能的影响，并对陶瓷介电机理进行初步的探讨，还应用凝胶注模成型工艺制作了 MCT 陶瓷微波器件。

分别采用 B_2O_3、LiF 和 B_2O_3-Bi_2O_3 添加对 $Ba_5Nb_4O_{15}$ 陶瓷进行低温烧结，并对低温烧结行为、显微结构以及微波介电性能进行研究。实验发现少量 B_2O_3、LiF 添加可有效降低 $Ba_5Nb_4O_{15}$ 陶瓷的烧结温度至 920℃左右；而 B_2O_3-Bi_2O_3 联合添加则随 Bi_2O_3 加入量的增加烧结温度先略有降低后升高；三种助剂均可在一定程度上改善 $Ba_5Nb_4O_{15}$ 陶瓷的谐振频率温度系数(τ_f)，同时也降低陶瓷的 $Q\times f$ 值。

对于 H_3BO_3 添加 $Ba_5Nb_4O_{15}$ 陶瓷，分别研究 V^{5+}和 Sb^{5+}取代 B 位 Nb^{5+}的结构与性能的影响。实验结果表明少量 V^{5+}、Sb^{5+}取代的 $Ba_5Nb_4O_{15}$ 陶瓷基本可以在 900℃左右烧结成瓷，并能有效调节 $Ba_5Nb_4O_{15}$ 陶瓷的 τ_f 值，其中 Sb^{5+}取代可以调节 $Ba_5Nb_4O_{15}$ 陶瓷的 τ_f 值接近于零。$Ba_5Nb_4O_{15}$ 陶瓷的 $Q\times f$ 值随 V^{5+}取代 Nb^{5+}量的增加先略有增加后下降；随 Sb^{5+}取代 Nb^{5+}量的增加先由 22,890GHz 升高至 34,630GHz 而后又降低，其中配方为 $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ (x=0.15)的陶瓷获得了较好的微波介电性能。为了进一步优化 $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ (x=0.15)陶瓷微波介电性能，采用正交实验优化 $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ (x=0.15)陶瓷的 H_3BO_3 加入量和部分制备工艺参数，加入 0.8wt% H_3BO_3 获得了最佳微波介电性能：ε_r=30.02，$Q\times f$=15,780GHz，τ_f=10ppm/℃，并能与 Ag 电极有较好的共烧相容性。

利用凝胶注模成型工艺，制作了复杂形状的微波陶瓷元器件，并对比干压成型与凝胶成型工艺对样品的微波介电性能的影响。此外，还成功制作实用化微波陶瓷片式天线。

论文最后探讨 $Ba_5Nb_4O_{15}$ 陶瓷的介电极化机理，得到调控微波陶瓷的电容率、谐振频率温度系数和介电损耗的一些经验。

关键词：微波介质陶瓷；$Ba_5Nb_4O_{15}$；低温烧结；介电性能；凝胶注模成型

Abstract

In this thesis, $Ba_5Nb_4O_{15}$ ceramics were prepared via conventional mixing oxide route, and the effects of sintering aid, ionic substitutions and processing factors on chemical structure and dielectric properties of the samples were systematically investigated. Dielectric mechanisms of the ceramic were also discussed in this thesis. In addition, gel-casting forming process was used to fabricate microwave components with complex shapes.

B_2O_3, LiF and B_2O_3-Bi_2O_3 were used as sintering additives to lower the sintering temperature for $Ba_5Nb_4O_{15}$ ceramics. Sintering behavior, microstructure and microwave properties were investigated by XRD, SEM, EDS and network analyzer. The results showed that a few amount of B_2O_3 or LiF could effectively lower the sintering temperature of $Ba_5Nb_4O_{15}$ ceramics into about 920℃. However, for the additions of B_2O_3-Bi_2O_3, the sintering temperature of $Ba_5Nb_4O_{15}$ ceramics was firstly decreased and then increased as the amount of Bi_2O_3 increased. The temperature coefficients of resonant frequency (τ_f) for $Ba_5Nb_4O_{15}$ ceramics was tuned effectively by the addition of B_2O_3, LiF and B_2O_3-Bi_2O_3, respectively. However, the $Q\times f$ values of the sample were decreased by those additions.

The effects of B-site substitution with V^{5+} ions or Sb^{5+} ions for Nb^{5+} ions on the structure and properties of $Ba_5Nb_4O_{15}$ ceramics were systematically studied. The results showed that with a small amount of substitution with V^{5+} ions or Sb^{5+} ions for Nb^{5+} ions, the $Ba_5Nb_4O_{15}$ ceramics could be sintered at about 900℃, and the τ_f value of ceramics could be effectively tuned toward to zero, especially for the substitution of Sb^{5+} ions for Nb^{5+} ions. The $Q\times f$ values of $Ba_5Nb_4O_{15}$ ceramics firstly increased slightly and then decreased for the substitution of V^{5+} ions for Nb^{5+} ions, and, increased firstly from 22,890GHz to 34,630GHz and then decreased with a increasing in the substitution of Sb^{5+} ions for Nb^{5+} ions. Best dielectric properties of $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ ceramics were obtained with a formula of $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ (x=0.15). In order to improve the dielectric properties of $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ further, the orthogonal design of experiment, $L_9(3^4)$, was used, in which the amount of H_3BO_3 and the processing parameters were considered as factors. The result showed $Ba_5(Nb_{1-x}Sb_x)_4O_{15}$ (x=0.15) ceramic added with 0.8wt% H_3BO_3 had a optimal dielectric properties of ε_r=30.02, $Q\times f$=15,780GHz, τ_f=10ppm/℃, in addition to good

chemical compatibility with silver electrodes.

Meanwhile, gel-casting forming process was successfully used to fabricate microwave components with complex shapes. The dielectric properties of ceramics prepared by gel-casting were compared with those by die-pressing. In addition, one kind of microwave antenna was also developed with the gel-casting forming process.

In the end of this thesis, dielectric polarization mechanism of $Ba_5Nb_4O_{15}$ ceramics was also discussed and useful hints for adjusting permittivity and temperature coefficient of resonant frequency for the ceramics were present.

Key words: Microwave dielectric ceramics; $Ba_5Nb_4O_{15}$; Low-temperature sintering; Dielectric properties; Gel-casting

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